



# Vibrational transition moments of CH<sub>4</sub> from first principles



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## ABSTRACT

New nine-dimensional (9D), *ab initio* electric dipole moment surfaces (DMSs) of methane in its ground electronic state are presented. The DMSs are computed using an explicitly correlated coupled cluster CCSD(T)-F12 method in conjunction with an F12-optimized correlation consistent basis set of the TZ-family. A symmetrized molecular bond representation is used to parameterise these 9D DMSs in terms of sixth-order polynomials. Vibrational transition moments as well as band intensities for a large number of IR-active vibrational bands of <sup>12</sup>CH<sub>4</sub> are computed by vibrationally averaging the *ab initio* dipole moment components. The vibrational wavefunctions required for these averages are computed variationally using the program TROVE and a new 'spectroscopic' <sup>12</sup>CH<sub>4</sub> potential energy surface. The new DMSs will be used to produce a hot line list for <sup>12</sup>CH<sub>4</sub>.

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## 1. Introduction

Methane plays an important role in atmospheric and astrophysical chemistry. Its rotation–vibration spectrum is of key importance for models of the atmospheres of bodies ranging from Titan to brown dwarfs. However the lack of precise data on methane spectra, particularly at higher temperatures, has severely limited models for atmospheres as diverse as Jupiter [1], exoplanets [2,3] and brown dwarfs [4]. Any temperature-dependent model of the methane spectrum requires a reliable treatment of the associated transition intensities. The construction of a reliable electric dipole moment surface (DMS) which can be used to generate such intensities concerns us in this paper.

Theoretically, a number of methane potential energy surfaces (PES) have been computed *ab initio* using different levels of theory [5–10]. The surface of Schwenke and Partridge [7] has been used in many benchmark studies as well as for accurate predictions of vibrational and ro-vibrational energies of CH<sub>4</sub>. However, to our knowledge no accurate and comprehensive *ab initio* DMSs of CH<sub>4</sub> have been published until recently. In some cases *ab initio* DMSs were used, but not actually provided, for example by Oyanagi et al. [9] (at the CCSD(T)/cc-pVTZ and MP2/cc-pVTZ level of theory) and Warmbier et al. [11] (RCCSD(T)/aug-cc-pVTZ). In 2012 Cassam-Chenai and Lievin [12] presented two reduced-dimension *ab initio* CH<sub>4</sub> DMSs computed at the MRCI/VQZ and MRCI/ACV5Z levels of theory, respectively on a small grid of 100 geometries and represented them as 3-dimensional Taylor polynomial expansions

in terms of normal coordinates. Most recently Nikitin et al. [13] computed *ab initio* DMSs of methane based on the CCSD(T)/cc-pCVQZ level of theory. The so-called molecular (MB) representation [8,14,15] was used to describe these DMSs analytically and to calculate integrated intensities for seven lower methane polyads, which were found to be in very good agreement with the experimental data. Rey et al. [16] employed these DMSs to simulate the room temperature absorption spectrum of <sup>12</sup>CH<sub>4</sub> in the infrared (IR) region. Comparison with experiment demonstrated both the accuracy of the predicted intensities as well as the quality of the underlying *ab initio* DMSs.

On the experimental side, electric transition dipole moments for CH<sub>4</sub> have been the subject of a large number of publications [17–27], where effective dipole moment parameters were derived either through fits to intensity measurements or using perturbation theory. The most recent and comprehensive collection of the effective dipole moment parameters describing excitations in the region up to 4800 cm<sup>−1</sup> was reported recently by Albert et al. [27]. Many of these studies also provide band intensities. Where possible we use these data to validate our vibrational transition moments as well as our DMSs.

The goal of this paper is to compute, from first principles, the vibrational transition moments and vibrational band intensities of <sup>12</sup>CH<sub>4</sub> for a large number of IR-active transitions in the range between 0 and 10000 cm<sup>−1</sup>. To this end we employed an explicitly correlated (F12) coupled cluster method in conjunction with an F12-optimized basis set to generate nine-dimensional (9D) DMSs of CH<sub>4</sub>. These surfaces are then vibrationally averaged over vibrational functions of <sup>12</sup>CH<sub>4</sub> computed through variationally solving the nuclear motion Schrödinger equation with the TROVE program [28]. This program has been used successfully for accurate and extensive ro-vibrational calculations on different tetratomic

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molecules [29–38]. The present work is the first application of TROVE to a larger system. Other variational approaches capable of treating this pentatomic molecule include the Lanczos-method developed by Carrington and Wang [39–42], MULTIMODE [43–46], and GENIUSH [47], as well as the methods of Halonen [48], Xie and Tennyson [49,50], Schwenke [51], and Nikitin [52]. The rigorous quantum dynamics algorithm employed by Yu [53,54] should be also mentioned as an alternative accurate approach employed for calculating vibrational energies of CH<sub>4</sub>.

The paper is structured as follows. In Section 2 the *ab initio* method used for generating DMSs of CH<sub>4</sub> is described and an analytical representation for these DMSs is introduced. The PES is detailed in Section 3. The variational approach is described in Section 4 and theoretical vibrational transition moments and band intensities are reported in Section 5. Finally, Section 6 offers some discussion and future prospects.

## 2. *Ab initio* calculations

We used the recently proposed explicitly correlated F12 coupled cluster method with single and double excitations including a perturbational estimate of connected triple excitations, CCSD(T)-F12c [55] in conjunction with the corresponding F12-optimized correlation-consistent basis sets, namely aug-cc-pVTZ-F12 [56] (augmented correlation-consistent polarized valence triple-zeta basis) as implemented in Molpro 2010 [57].

Methane has nine vibrational degrees of freedom and thus requires a very extensive grid of geometries in the *ab initio* calculations. We have computed three *ab initio* DMSs (one for each Cartesian component) on a fine grid of 114000 geometries covering the energy range up to 50000 cm<sup>−1</sup> with C–H distances ranging from 0.75 to 2.0 Å, and interbond angles ranging from 50° to 140°. The central finite difference scheme with an added external dipole field of 0.005 a.u. was used to compute the dipole moment component as first derivatives with respect to the external electric field in the dipole approximation.

In order to represent the *ab initio* dipole moment vector  $\boldsymbol{\mu}$  of CH<sub>4</sub> analytically we use the so-called symmetrized molecular bond (SMB) representation [8], where  $\boldsymbol{\mu}$  is projected onto three symmetrized combinations of vectors associated with the four molecular bonds C–H<sub>*i*</sub> (*i* = 1, 2, 3, 4). An analogous approach was used to represent the *ab initio* dipole moment of NH<sub>3</sub> [58] (see also Refs. [8,13] for non-symmetrized MB representations of methane DMSs). The three components of the dipole moment of CH<sub>4</sub> span three components of the F<sub>2</sub> irreducible representation ( $\Gamma = F_{2x}, F_{2y}, \text{ or } F_{2z}$ ) of the T<sub>d</sub>(M) molecular symmetry group [59]. We define the following three symmetrically independent reference vectors  $\mathbf{n}_r$  spanning the same representation F<sub>2</sub>:

$$\mathbf{n}_{F_{2x}} = \frac{1}{2} \left( \frac{\mathbf{r}_1}{|\mathbf{r}_1|} - \frac{\mathbf{r}_2}{|\mathbf{r}_2|} + \frac{\mathbf{r}_3}{|\mathbf{r}_3|} - \frac{\mathbf{r}_4}{|\mathbf{r}_4|} \right), \quad (1)$$

$$\mathbf{n}_{F_{2y}} = \frac{1}{2} \left( \frac{\mathbf{r}_1}{|\mathbf{r}_1|} - \frac{\mathbf{r}_2}{|\mathbf{r}_2|} - \frac{\mathbf{r}_3}{|\mathbf{r}_3|} + \frac{\mathbf{r}_4}{|\mathbf{r}_4|} \right), \quad (2)$$

$$\mathbf{n}_{F_{2z}} = \frac{1}{2} \left( \frac{\mathbf{r}_1}{|\mathbf{r}_1|} + \frac{\mathbf{r}_2}{|\mathbf{r}_2|} - \frac{\mathbf{r}_3}{|\mathbf{r}_3|} - \frac{\mathbf{r}_4}{|\mathbf{r}_4|} \right), \quad (3)$$

where  $\mathbf{r}_i$  is a molecular bond vector pointing from C to H<sub>*i*</sub> (*i* = 1, 2, 3, 4). The dipole moment vector  $\boldsymbol{\mu}$  can now be represented as

$$\boldsymbol{\mu} = \mathbf{n}_{F_{2x}} \mu_{F_{2x}} + \mathbf{n}_{F_{2y}} \mu_{F_{2y}} + \mathbf{n}_{F_{2z}} \mu_{F_{2z}}, \quad (4)$$

where the projections  $\mu_{F_{2\alpha}}$  ( $\alpha = x, y, z$ ) are the dipole moment functions also spanning the F<sub>2</sub> representation. Each component  $\mu_{F_{2x}}$  is then expanded as

$$\mu_{F_{2x}} = \sum_{i_1, i_2, \dots, i_9} \mu_{i_1, i_2, \dots, i_9}^{\alpha} \xi_1^{i_1} \xi_2^{i_2} \dots \xi_9^{i_9}, \quad (5)$$

in terms of the following set of nine independent internal coordinates:

$$\xi_i = (r_i - r_e) e^{-\beta(r_i - r_e)^2}, \quad i = 1, 2, 3, 4, \quad (6)$$

$$\xi_5 = \frac{1}{\sqrt{12}} (2\alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{24} + 2\alpha_{34}), \quad (7)$$

$$\xi_6 = \frac{1}{2} (\alpha_{13} - \alpha_{14} - \alpha_{23} + \alpha_{24}), \quad (8)$$

$$\xi_7 = \frac{1}{\sqrt{2}} (\alpha_{24} - \alpha_{13}), \quad (9)$$

$$\xi_8 = \frac{1}{\sqrt{2}} (\alpha_{23} - \alpha_{14}), \quad (10)$$

$$\xi_9 = \frac{1}{\sqrt{2}} (\alpha_{34} - \alpha_{12}), \quad (11)$$

where  $r_i$  are the bond lengths and  $\alpha_{ij}$  are the interbond angles. The coordinate transformation from the six bending coordinates  $\alpha_{ij}$  to the five independent coordinates  $\xi_5, \xi_6, \xi_7, \xi_8$ , and  $\xi_9$  defined by Eqs. (7)–(11) has to be complemented by the redundancy condition [48]:

$$\begin{vmatrix} 1 & \cos \alpha_{12} & \cos \alpha_{13} & \cos \alpha_{14} \\ \cos \alpha_{12} & 1 & \cos \alpha_{23} & \cos \alpha_{24} \\ \cos \alpha_{13} & \cos \alpha_{23} & 1 & \cos \alpha_{34} \\ \cos \alpha_{14} & \cos \alpha_{24} & \cos \alpha_{34} & 1 \end{vmatrix} = 0. \quad (12)$$

It should be noted that Taylor-type expansions like Eq. (5) can lead to non-physical behaviour at large angle displacements. Following Hollenstein et al. [60], we have introduced the factor  $\exp(-\beta(r_i - r_e)^2)$  in order to keep the expansion in Eq. (5) from diverging at large  $r_i$ . Here  $r_e$  is a reference expansion center which is conveniently taken at a value close to the molecular equilibrium. Eq. (5) cannot guarantee correct behaviour at large displacements of the inter-bond angle, for example at  $\alpha_{ij} \rightarrow 180^\circ$ . Such geometries correspond to very high energies with negligibly small probability density and thus are never accessed in our approach. However this could be a problem for variational methods based on quadratures that often require explicit values of the DMSs or PES at very large ranges of geometries.

The properties of the components  $\mu_{F_{2x}}$  associated with F<sub>2</sub> impose symmetry relations between the expansion coefficients  $\mu_{i_1, \dots, i_9}^{\alpha}$ . These relations can be reconstructed by applying the standard symmetry transformation rules [59,61] between the F<sub>2x</sub>, F<sub>2y</sub>, F<sub>2z</sub> components of F<sub>2</sub>. We employed the Maple program function ‘solve’ to find a set of independent coefficients  $\mu_{i_1, \dots, i_9}^{\alpha}$  by solving an over-determined system of linear equations (see Ref. [15] for details on the computational procedure). For example, to first order the dipole moment functions  $\mu_x$  are given by the expansions

$$\mu_{F_{2x}} = \mu_7 \xi_7 + \mu_1 (\xi_1 - \xi_2 + \xi_3 - \xi_4) + O(\xi_k^2) \dots, \quad (13)$$

$$\mu_{F_{2y}} = \mu_7 \xi_8 + \mu_1 (\xi_1 - \xi_2 - \xi_3 + \xi_4) + O(\xi_k^2) \dots, \quad (14)$$

$$\mu_{F_{2z}} = \mu_7 \xi_9 + \mu_1 (\xi_1 + \xi_2 - \xi_3 - \xi_4) + O(\xi_k^2) \dots, \quad (15)$$

where the shorthand notations  $\mu_7 = \mu_{0,0,0,0,0,0,1,0,0}^{\alpha}$  and  $\mu_1 = \mu_{1,0,0,0,0,0,0,0,0}^{\alpha}$  are used. The complete expansion set is given in the [Supplementary Material](#) to this paper. A full sixth-order symmetrized expansion requires 680 symmetrically independent dipole moment parameters in total. Taking into account the symmetry relations, the expansion Eq. (5) can be written as:

$$\mu_{\alpha} = \sum_{i_1, i_2, \dots, i_9} \mu_{i_1, i_2, i_3, \dots, i_9}^{\alpha} \{ \xi_1^{i_1} \xi_2^{i_2} \dots \xi_9^{i_9} \}^{F_{2\alpha}}, \quad (16)$$

where  $\{\xi_1^{i_1} \xi_2^{i_2} \dots \xi_9^{i_9}\}^{F_{2x}}$  is a symmetrized combination of different permutations of the internal coordinates consistent with  $T_d(M)$  group operations and spanning the  $F_{2x}$  symmetry.

The actual values of expansion parameters  $\mu_{i_1, i_2, i_3, \dots, i_9}^z$  corresponding to our *ab initio* DMSs were determined through a joint least-squares fit to all  $3 \times 114000$  *ab initio* dipole moment values simultaneously. Some parameters with large standard errors that exhibit strong correlation were constrained to zero. The *ab initio* data in these fits were weighted using the following expression proposed by Partridge and Schwenke [62]:

$$w_i = N \times \frac{\tanh[-0.0004 \text{ cm} \times (V_i - 18000 \text{ cm}^{-1})] + 1.00000002}{2.00000002}, \quad (17)$$

where  $N$  is a normalization factor defined by  $\sum_i w_i = 1$  and  $V_i$  is the corresponding *ab initio* energy at the  $i$ th geometry (in  $\text{cm}^{-1}$ ), measured relative to the equilibrium energy and computed using the same level of theory. The *ab initio* energy  $V_i$  is weighted by the factor  $w_i$  in the PES fitting; these weight factors favor the energies below  $18000 \text{ cm}^{-1}$ . In the end 296 parameters were needed to obtain a weighted ( $w_i$ ) root-mean-squares (rms) error of 0.00016 D. The expansion parameters are given in the [Supplementary Material](#) of the paper along with a Fortran 95 routine incorporating the corresponding analytical form.

### 3. Potential energy surface

In this work we use a new ‘spectroscopic’ PES generated as follows. First, an *ab initio* PES was generated on the same grid of 114000 geometries employing the same CCSD(T)-F12c approach [55] used for the DMSs, but with the larger aug-cc-pVQZ-F12 basis set [56]. The frozen core approximation was applied in the coupled cluster calculations. We did not include core-valence corrections and higher-order coupled cluster corrections because they cancel to a large extent (see the work by Yachmenev et al. [33]), and also because this would be computationally very costly. Relativistic corrections were computed using the second-order Douglas-Kroll method as implemented in Molpro 2010. With this method we obtained the equilibrium bond length  $r_e = 1.08734 \text{ \AA}$ , which is close to the value  $r_e = 1.08595 \text{ \AA}$  derived in a combined experimental/*ab initio* analysis [63]. The *ab initio* potential energies have been represented using a symmetrized analytical expansion in terms of the four stretching coordinates  $1 - \exp(-a(r_i - r_e))$  ( $i = 1, 2, 3, 4$ ) and five bending coordinates  $\xi_j$  ( $j = 5, 6, 7, 8, 9$ ) from Eqs. (6)–(11). The symmetry relations between potential parameters in the  $T_d(M)$  group were derived employing Maple with the procedure described above. In total 287 symmetrically independent parameters are needed for a full sixth-order expansion. These expansion parameters were obtained from a fitting procedure using the weighting scheme given in Eq. (17). Some parameters showing large standard errors were constrained to zero, which resulted in 268 potential parameters needed to get a weighted rms error of  $0.3 \text{ cm}^{-1}$ .

To improve the quality of the *ab initio* PES, we slightly refined it by fitting to the ‘experimental’ energies of  $^{12}\text{CH}_4$  extracted from the HITRAN 2008 [64] database for  $J = 0, 1, 2, 3, 4$ . In the refinement the fitted PES was constrained to follow closely the shape of the initial *ab initio* PES of  $\text{CH}_4$  in order to guarantee that the PES retains a physically correct shape. This was achieved by simultaneously fitting the refined force constants to the *ab initio* points and to the experimental energy levels [65]. This procedure also allows all potential parameters to be varied irrespective of any shortage of experimental data. By optimizing all 268 potential parameters defining the PES, we improved the observed-minus-calculated energies for  $J \leq 4$  to have a root-mean-square (rms)

error of only  $0.1 \text{ cm}^{-1}$ . This compares with an rms error of about  $4 \text{ cm}^{-1}$  obtained with the initial *ab initio* PES for the same set of experimental data. The fitting approach is described in detail by Yurchenko et al. [66] and implemented in the variational program TROVE [28]. This new ‘spectroscopic’ PES for  $^{12}\text{CH}_4$  will be the subject of further improvements and a future publication. Both the initial *ab initio* and refined potential parameters are given as [Supplementary Material](#) along with a fortran 95 program containing the corresponding potential energy function.

### 4. Variational calculations

The vibrational wavefunctions and energies of  $^{12}\text{CH}_4$  were calculated using the variational program TROVE [28]. In this approach the Hamiltonian operator is represented as an expansion around a reference geometry taken presently at the molecular equilibrium. The kinetic energy operator is expanded in terms of the nine linearized coordinates  $\xi_i^\ell$ , which are linearized versions of the internal coordinates  $\xi_i$  ( $i = 1, \dots, 9$ ) defined above; for the potential energy function we use  $1 - \exp(-a\xi_i^\ell)$  ( $i = 1, 2, 3, 4$ ) for the four stretching and  $\xi_j^\ell$  ( $j = 5, 6, 7, 8, 9$ ) for the five bending linearized coordinates. The latter expansions were applied to the refined PES introduced above. The kinetic and potential energy parts were truncated after the sixth and eighth order, respectively.

To construct the basis set, TROVE employs a multi-step contraction scheme based on the following polyad truncation. The polyad number in case of  $\text{CH}_4$  is given by

$$P = 2(v_1 + v_2 + v_3 + v_4) + v_5 + v_6 + v_7 + v_8 + v_9, \quad (18)$$

where  $v_i$  is a vibrational quantum number associated with a one-dimensional primitive basis function  $\phi_{v_i}(\xi_i^\ell)$  ( $i = 1, 2, 3, \dots, 9$ ). At Step 1, nine sets of  $\phi_{v_i}(\xi_i^\ell)$  are generated using the Numerov-Cooley [67,68] method by solving the 1D Schrödinger equations for each of the nine modes separately. The corresponding 1D Hamiltonian operators are obtained from the 9D Hamiltonian operator ( $J = 0$ ) by freezing all but one vibrational coordinates at their equilibrium values. At Step 2 the 9D coordinate space is divided into the three reduced sub-spaces, (i)  $\{\xi_1^\ell, \xi_2^\ell, \xi_3^\ell, \xi_4^\ell\}$ , (ii)  $\xi_5^\ell, \xi_6^\ell$ , and (iii)  $\xi_7^\ell, \xi_8^\ell, \xi_9^\ell$ . The goal of this second step is twofold: (a) to improve the basis set by making it more compact and (b) to prepare the basis functions in a symmetrized representation. The division into the sub-spaces is thus dictated by the  $T_d(M)$  symmetry: each of the sub-spaces is symmetrically independent and thus can be processed separately. For each of these sub-spaces, the Schrödinger equations are solved for the corresponding reduced Hamiltonian operators employing as basis the products of the corresponding primitive functions  $\phi_{v_i}(\xi_i^\ell)$  generated at Step 1. The sub-space bases are truncated using the condition  $P \leq P_{\max}$ , where  $P$  is given by Eq. (18). In this work we use  $P_{\max} = 12$ , i.e. our reduced sub-space basis sets are defined by

$$v_1 + v_2 + v_3 + v_4 \leq 6, \quad (19)$$

$$v_5 + v_6 \leq 12, \quad (20)$$

$$v_7 + v_8 + v_9 \leq 12. \quad (21)$$

The three sets of eigenfunctions  $\Psi_{\lambda_1}^{(i)}(\xi_1^\ell, \xi_2^\ell, \xi_3^\ell, \xi_4^\ell)$ ,  $\Psi_{\lambda_2}^{(ii)}(\xi_5^\ell, \xi_6^\ell)$ , and  $\Psi_{\lambda_3}^{(iii)}(\xi_7^\ell, \xi_8^\ell, \xi_9^\ell)$  resulting from these solutions are symmetrized and assigned local mode quantum numbers (i)  $v_1, v_2, v_3, v_4$ , (ii)  $v_5, v_6$ , and (iii)  $v_7, v_8, v_9$  and vibrational symmetry  $\Gamma_{\text{vib}}$ . The final vibrational basis set is formed from products  $\Psi_{\lambda_1}^{(i)} \times \Psi_{\lambda_2}^{(ii)} \times \Psi_{\lambda_3}^{(iii)}$ , which are contracted with  $P \leq 12$  and symmetrized again using the standard technique for transformations to irreducible representations (see, for example, Ref. [59]). Thus our contracted vibrational basis set consists of ten symmetrically independent groups, one for each irreducible representation of the  $T_d(M)$  group  $A_1, A_2, E_a, E_b, F_{1x}, F_{1y}, F_{1z}, F_{2x}, F_{2y}, F_{2z}$ . Only the first

component is processed from the degenerate symmetries  $E$ ,  $F_1$ , and  $F_2$ . Therefore only five vibrational Hamiltonian matrices (one for each symmetry) are constructed and diagonalized. In the diagonalizations we use the eigensolver DSYEV from LAPACK as implemented in the MKL libraries. The dimensions of the matrices to be diagonalized are 2190, 1725, 3901, 5481, and 5940 for  $A_1$ ,  $A_2$ ,  $E$ ,  $F_1$ , and  $F_2$ , respectively. The results are collected in Tables 1–3, where the calculated energies are also compared with the available experimental values from [27,69–71]. It should be noted that our basis set with  $P \leq 12$  does not provide fully converged energies. The same comment applies to our new ‘spectroscopic’ PES: because of the limitations of the method, this PES can only guarantee the energies given in Table 1 when used with the same approach and basis set employed in the refinements, i.e.  $P_{\max} = 12$ . However the vibrational transition moments reported in the next section appear to be rather insensitive to the size of the basis set and the shape of the potential (see below).

## 5. Transition moments

The transition moment connecting two states  $i$  (‘initial’) and  $f$  (‘final’) can be defined as the vibrational average of a dipole moment component  $\mu_\alpha$  ( $\alpha = x, y, z$ ):

$$\bar{\mu}_\alpha^{(i,f)} = \langle \Psi_i^{\Gamma_i} | \mu_\alpha | \Psi_f^{\Gamma_f} \rangle, \quad (22)$$

where  $\mu_\alpha$  ( $\alpha = x, y, z$ ) are the Cartesian components of the dipole moment in the molecule-fixed frame (defined in TROVE by the Eckart conditions [72]);  $\Psi_i^{\Gamma_i}$  and  $\Psi_f^{\Gamma_f}$  are vibrational eigenfunctions obtained variationally, and  $\Gamma_s$  represents a component of one of the ten irreducible representations  $A_1$ ,  $A_2$ ,  $E$ ,  $E_g$ ,  $F_{1x}$ ,  $F_{1y}$ ,  $F_{1z}$ ,  $F_{2x}$ ,  $F_{2y}$ ,  $F_{2z}$  of  $T_d(M)$ . It should be noted that the transition moments defined by Eq. (22) depend on the choice of the molecular-fixed coordinate system [73] as well as on the particular choice of the transformational properties of the irreducible representations  $E$ ,  $F_1$ , and  $F_2$  (we use irrep-matrices from Hougen’s monograph [74]). The following quantity, averaged over the Cartesian components  $\alpha = x, y, z$  and any degenerate components of the wavefunctions, is independent of these choices:

$$\bar{\mu}^{if} \equiv \bar{\mu}^{(i,f)} = \sqrt{[\bar{\mu}_x^{(i,f)}]^2 + [\bar{\mu}_y^{(i,f)}]^2 + [\bar{\mu}_z^{(i,f)}]^2}, \quad (23)$$

where

$$\bar{\mu}_\alpha^{(i,f)} = \sum_{a,b} \mu_{\alpha}^{(i,f,a,b)}, \quad (24)$$

and the vibrational transition moment  $\bar{\mu}^{if}$  is defined as the length of the vector  $[\bar{\mu}_x^{(i,f)}, \bar{\mu}_y^{(i,f)}, \bar{\mu}_z^{(i,f)}]$ .

A number of calculated values of the vibrational transition moments  $\bar{\mu}^{if}$  as well as matrix elements  $\bar{\mu}_\alpha^{(i,f)}$  of  $^{12}\text{CH}_4$

**Table 1**

Vibrational transition moments,  $\bar{\mu}^{if}$  in D, individual matrix elements  $\bar{\mu}_\alpha^{(i,f)}$  (D), and band intensities,  $S_{if}$  in  $\text{cm}^{-1} \text{atm}^{-2}$ , for  $^{12}\text{CH}_4$  for transitions from the vibrationally ground state. The calculated and experimentally derived term values  $E_f$  of the upper states are given in  $\text{cm}^{-1}$ .

$\Gamma$	State-f	$E_f^{\text{obs}}$	$E_f^{\text{calc}}$	$\bar{\mu}_x^{(i,f)}$	$\bar{\mu}^{if}_{\text{calc}}$	$S_{if}^{\text{(calc)}}$	$S_{if}^{\text{(obs)}} [27]$
$F_2$	0 0 0 1	1310.76	1310.87	−0.05676	0.09831	129.323	127.68
$F_2$	0 0 0 2	2614.26	2614.32	0.00408	0.00706	1.334	1.05
$F_2$	0 1 0 1	2830.32	2830.28	0.01038	0.01797	9.346	6.63 <sup>a</sup>
$F_2$	0 0 1 0	3019.49	3019.49	−0.05410	0.09370	271.062	269.92
$F_2$	0 0 0 3	3870.49	3870.49	−0.00231	0.00401	0.636	0.59 <sup>b</sup>
$F_2$	0 0 0 3	3930.92	3930.81	0.00166	0.00288	0.332	0.14 <sup>b</sup>
$F_2$	0 1 0 2	4142.86	4142.99	−0.00171	0.00295	0.370	0.34
$F_2$	1 0 0 1	4223.46	4223.52	0.00775	0.01343	7.791	7.84
$F_2$	0 0 1 1	4319.21	4319.43	−0.00919	0.01593	11.201	10.24
$F_2$	0 2 0 1	4348.72	4348.97	−0.00145	0.00252	0.281	0.55 <sup>c</sup>
$F_2$	0 2 0 1	4378.95	4379.15	−0.00013	0.00023	0.002	0.23 <sup>c</sup>
$F_2$	0 1 1 0	4543.76	4543.90	0.00392	0.00678	2.138	1.26 <sup>d</sup>
$F_2$	0 0 0 4	5143.24	5143.25	0.00035	0.00060	0.019	0.01 <sup>e</sup>
$F_2$	0 0 0 4	5211.29	5210.65	−0.00021	0.00037	0.007	
$F_2$	0 1 0 3	5370.52	5370.37	−0.00014	0.00023	0.003	
$F_2$	0 1 0 3	5429.58	5429.07	−0.00058	0.00101	0.056	
$F_2$	0 1 0 3	5445.12	5444.87	0.00011	0.00020	0.002	
$F_2$	1 0 0 2		5519.47	0.00011	0.00019	0.002	
$F_2$	0 0 1 2	5588.03	5586.76	0.00156	0.00270	0.416	
$F_2$	0 0 1 2		5620.63	−0.00074	0.00129	0.095	
$F_2$	0 0 1 2		5633.69	−0.00102	0.00176	0.179	
$F_2$	0 2 0 2	5643.45	5643.64	0.00005	0.00009	0.000	
$F_2$	0 2 0 2	5668.60	5668.70	−0.00027	0.00047	0.013	
$F_2$	1 1 0 1		5727.16	0.00016	0.00028	0.005	
$F_2$	0 1 1 1	5823.10	5823.03	−0.00213	0.00368	0.808	
$F_2$	0 1 1 1	5844.00	5843.72	−0.00052	0.00089	0.048	
$F_2$	1 0 1 0		5861.92	−0.00031	0.00054	0.018	
$F_2$	0 3 0 1	5867.66	5868.23	−0.00026	0.00046	0.012	
$F_2$	0 3 0 1	5894.12	5894.54	−0.00007	0.00013	0.001	
$F_2$	0 0 2 0	6004.69	6004.45	−0.00301	0.00522	1.671	1.63 <sup>e</sup>
$F_2$	0 2 1 0	6054.64	6054.67	−0.00055	0.00094	0.055	
$F_2$	0 2 1 0	6065.32	6065.26	−0.00055	0.00095	0.056	

<sup>a</sup> The total intensity of the  $\nu_2 + \nu_4$  band,  $9.94 \text{ cm}^{-1} \text{atm}^{-2}$  Albert et al. [27], which includes both  $F_1$  and  $F_2$  sub-components agrees well with our  $S_{0101F_2}^{\text{(calc)}}$  value.  
<sup>b</sup> The total intensity of the  $3\nu_4$  band,  $0.83 \text{ cm}^{-1} \text{atm}^{-2}$  Albert et al. [27], which includes  $A_1$  and  $F_1$  sub-components in addition to two  $F_2$  ones can be compared to the sum of the two ‘calc’ band intensities  $S_{0003F_2}^{\text{(calc)}}$ .  
<sup>c</sup> The total intensity of the  $2\nu_2 + \nu_4$  band which includes three sub-bands ( $F_1$ ,  $F_2$  and  $F_2$ ) by Albert et al. [27] is  $0.93 \text{ cm}^{-1} \text{atm}^{-2}$ . Hilico et al. [25] reported somewhat smaller value of  $0.63 \text{ cm}^{-1} \text{atm}^{-2}$ , which suggests a better agreement with our value for the  $F_2$  sub-band only.  
<sup>d</sup> Compare to the estimate by Hilico et al. [19],  $1.84 \text{ cm}^{-1} \text{atm}^{-2}$ , which is closer to our value.  
<sup>e</sup> As estimated by Robert et al. [26].



**Table 2**

Vibrational transition moments,  $\bar{\mu}^{if}$  in D, individual matrix elements  $\bar{\mu}_x^{(i,f;\alpha;\beta)}$  ( $\alpha = x, y, z$  or  $a, b$  and  $\beta = x, y, z$ ) in D, and band intensities,  $S_{if}$  in  $\text{cm}^{-1} \text{atm}^{-2}$ , for  $^{12}\text{CH}_4$  for the transitions from the  $v_4$  state. The calculated and experimentally derived term values  $\bar{E}_i$  of the upper states are given in  $\text{cm}^{-1}$ .

$\Gamma_f$	State-f	$\bar{E}_f^{\text{obs}}$	$\bar{E}_f^{\text{calc}}$	$\bar{\mu}_x^{(i,\Gamma_\alpha;f,F_2\beta)}$	$\alpha$	$\beta$	$\bar{\mu}_{\text{calc}}^{if}$	$S_{if}^{(\text{calc})}$	$S_{if}^{(\text{obs})}$ [22]
$E$	0 1 0 0	1533.33	1533.39	-0.00406	$a$	$z$	0.00704	0.00013	
$A_1$	0 0 0 2	2587.04	2586.98	0.05046		$z$	0.08741	0.17802	} 0.931 <sup>a</sup>
$F_2$	0 0 0 2	2614.26	2614.32	0.05718	$y$	$x$	0.14006	0.46701	
$E$	0 0 0 2	2624.62	2624.61	0.06530	$a$	$z$	0.11310	0.30697	
$F_2$	0 1 0 1	2830.32	2830.28	0.00641	$y$	$x$	0.01569	0.00684	0.00872
$F_1$	0 1 0 1	2846.07	2846.06	0.00007	$z$	$x$	0.00016	0.000001	
$A_1$	1 0 0 0	2916.48	2916.54	0.00236		$z$	0.00408	0.00049	0.000689
$F_2$	0 0 1 0	3019.49	3019.49	-0.01675	$a$	$z$	0.04104	0.05265	0.0481
$A_1$	0 2 0 0	3063.65	3063.61	-0.00088	$z$	$z$	0.00153	0.00007	0.0005
$E$	0 2 0 0	3065.14	3065.12	0.00144	$a$	$z$	0.00250	0.00020	
$F_2$	0 0 0 3	3870.49	3870.49	-0.00383	$a$	$z$	0.00938	0.00412	
$A_1$	0 0 0 3	3909.20	3909.68	-0.00424		$z$	0.00734	0.00256	
$F_1$	0 0 0 3	3920.51	3920.15	-0.00320	$z$	$x$	0.00784	0.00293	
$F_2$	0 0 0 3	3930.92	3930.81	-0.00299	$a$	$z$	0.00732	0.00257	
$E$	0 1 0 2	4101.39	4101.49	-0.00973	$a$	$z$	0.01685	0.01451	
$F_1$	0 1 0 2	4128.76	4128.73	0.00890	$z$	$x$	0.02180	0.02451	
$A_1$	0 1 0 2	4132.86	4132.83	0.00923		$z$	0.01599	0.01320	
$F_2$	0 1 0 2	4142.86	4142.99	-0.00537	$a$	$z$	0.01315	0.00897	
$E$	0 1 0 2	4151.21	4151.28	0.00525	$a$	$z$	0.00910	0.00430	
$F_2$	1 0 0 1	4223.46	4223.52	0.00244	$a$	$z$	0.00597	0.00190	
$F_2$	0 0 1 1	4319.21	4319.43	-0.03798	$a$	$z$	0.09303	0.47649	
$E$	0 0 1 1	4322.18	4322.21	-0.04272	$a$	$z$	0.07399	0.30170	
$A_1$	0 0 1 1	4322.70	4322.40	-0.03326		$z$	0.05761	0.18292	
$F_1$	0 0 1 1	4322.59	4322.66	-0.03760	$z$	$x$	0.09211	0.46758	
$F_2$	0 2 0 1	4348.72	4348.97	-0.00451	$a$	$z$	0.01104	0.00678	
$F_1$	0 2 0 1	4363.61	4363.61	0.00076	$z$	$x$	0.00186	0.00019	
$F_2$	0 2 0 1	4378.95	4379.15	-0.00057	$a$	$z$	0.00140	0.00011	
$E$	1 1 0 0	4435.12	4435.18	-0.00095	$a$	$z$	0.00165	0.00015	
$F_1$	0 1 1 0	4537.55	4537.75	0.00143	$z$	$x$	0.00351	0.00073	
$F_2$	0 1 1 0	4543.76	4543.90	-0.00121	$a$	$z$	0.00297	0.00052	
$E$	0 3 0 0	4592.03	4592.12	-0.00030	$a$	$z$	0.00052	0.00002	
$A_1$	0 3 0 0	4595.51	4595.66	0.00000		$z$	0.00000	0.00000	

corresponding to transitions from the three lowest vibrational states ( $v_0, v_2$ , and  $v_4$ ) are listed in Tables 1–3. The non-zero matrix elements  $\bar{\mu}_x^{(i,\Gamma';f,\Gamma'')}$  in Tables 1–3 for each transition satisfy the following set of relations:

$$\begin{aligned}
 \bar{\mu}_x^{(A_1;F_{2z})} &= -\bar{\mu}_y^{(A_1;F_{2x})} = -\bar{\mu}_z^{(A_1;F_{2y})}, \\
 \bar{\mu}_x^{(F_{2x};F_{2y})} &= -\bar{\mu}_y^{(F_{2y};F_{2z})} = -\bar{\mu}_z^{(F_{2x};F_{2z})}, \\
 \bar{\mu}_x^{(F_{2x};E_a)} &= 2\bar{\mu}_y^{(F_{2x};E_a)} = -\frac{2}{\sqrt{3}}\bar{\mu}_y^{(F_{2x};E_b)} = 2\bar{\mu}_z^{(F_{2y};E_a)} = \frac{2}{\sqrt{3}}\bar{\mu}_z^{(F_{2z};E_b)}, \\
 \bar{\mu}_x^{(F_{2x};F_{1z})} &= -\bar{\mu}_y^{(F_{2y};F_{1y})} = -\bar{\mu}_y^{(F_{2y};F_{1x})} = \bar{\mu}_y^{(F_{2y};F_{1z})} = \bar{\mu}_z^{(F_{2z};F_{1x})} = -\bar{\mu}_z^{(F_{2z};F_{1y})}, \\
 \bar{\mu}_x^{(F_{1x};E_b)} &= \frac{2}{\sqrt{3}}\bar{\mu}_y^{(F_{1y};E_a)} = 2\bar{\mu}_y^{(F_{1y};E_b)} = -\frac{2}{\sqrt{3}}\bar{\mu}_z^{(F_{1z};E_a)} = 2\bar{\mu}_z^{(F_{1z};E_b)},
 \end{aligned} \quad (25)$$

where indices  $i, f$  are omitted for simplicity. Therefore Tables 1–3 list only one value for each pair of states. A complete list of 47861 vibrational transition moments and matrix elements  $\bar{\mu}_x^{(i,\Gamma';f,\Gamma'')}$  of  $^{12}\text{CH}_4$  is provided as Supplementary Material for all allowed transitions in the frequency range from 0 to 10000  $\text{cm}^{-1}$  with lower state energies below 5000  $\text{cm}^{-1}$ .

Because of the high symmetry of methane many vibrational transition moments  $\bar{\mu}^{if}$  vanish. For example,  $\bar{\mu}^{if} = 0$  between  $A_1$  eigenfunctions of the ground vibrational state (GS) and any vibrational states of  $A_1, A_2, E$ , and  $F_1$  symmetry. This includes

transitions within the GS and the transitions giving rise to the fundamental bands  $v_1(A_1)$  and  $v_2(E)$ . All these transitions have zero vibrational transition moments and are thus dipole forbidden. Certainly this does not rule out ro-vibrational transitions within these bands, although such transitions are often also referred to as ‘forbidden’. At a formal level any transitions connecting rotation-vibration states with the correct symmetries are allowed [75,76]. In practice, centrifugal distortions arising from rotation–vibration interactions can introduce  $F_2$ -vibrational contributions into, for example, the GS rotational wavefunctions, thus producing non-zero ro-vibrational line strengths. Conversely, ‘allowed’ ro-vibrational transitions are based only on non-zero vibrational transition moments  $\bar{\mu}_x^{(i,f;\alpha;\beta)}$ , such as the ones given in Tables 1–3.

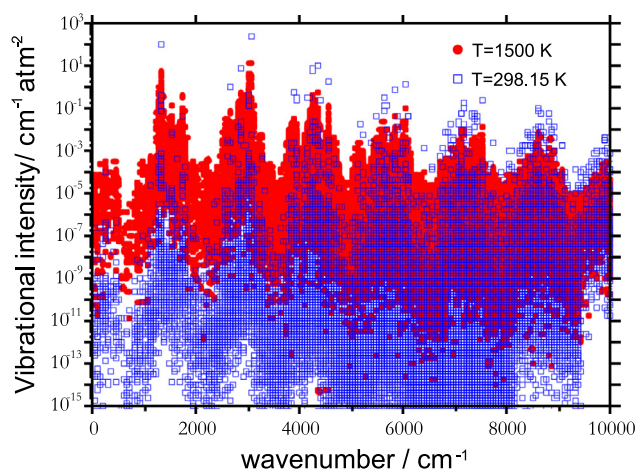
The transition moments presented here can be used to derive the effective dipole moment parameters of  $^{12}\text{CH}_4$ , which are important for modelling intensities of this molecule (see Ref. [27] for the most recent collection of the effective dipole moment parameters). Examples of such an exercise can be found in Refs. [23,77]. For example, the parameter  $V_{0000A_1-0001F_2}^{(0,0A_1)} = 0.098677(88)$  D [27] is in good agreement with our value  $\sqrt{3}\bar{\mu}_x^{(g,s,A_1;v_4,F_2)} = 0.098314$  D. Similarly,  $V_{0000A_1-0010F_2}^{(0,0A_1)} = -0.094622(47)$  D [27] agrees well with our value  $\sqrt{3}\bar{\mu}_x^{(g,s,A_1;v_3,F_2)} = 0.093699$  D (see Table 1). Here  $\sqrt{3}$  is a conversion factor associated with the Dyad-GS and Pentad-GS zero-order effective dipole constants in the tensorial representation (see, for

**Table 3**

Vibrational transition moments,  $\bar{\mu}^{if}$  in D, individual matrix elements  $\bar{\mu}_x^{(i,T_{\alpha f}, E_{\beta})}$  ( $\alpha = x, y, z$  and  $\beta = a, b$ ) in D, and band intensities,  $S_{if}$  in  $\text{cm}^{-1} \text{atm}^{-2}$ , for  $^{12}\text{CH}_4$  for the transitions from the  $v_2$  state. The calculated and experimentally derived term values  $E_i$  of the upper states are given in  $\text{cm}^{-1}$ .

$\Gamma_f$	State-f	$E_{\text{obs}}$	$E_{\text{calc}}$	$\bar{\mu}_x^{(i,T_{\alpha f}, E_{\beta})}$	$\alpha$	$\beta$	$\bar{\mu}_{\text{calc}}^{if}$	$S_{if}^{(\text{calc})}$	$S_{if}^{(\text{obs})}$ [22]
$F_2$	0 0 0 2	2614.26	2614.32	0.00110	$z$	$a$	0.00191	0.00002	0.00008
$F_2$	0 1 0 1	2830.32	2830.28	−0.05740	$z$	$a$	0.09942	0.08000	} 0.145 <sup>a</sup>
$F_1$	0 1 0 1	2846.07	2846.06	−0.05718	$x$	$b$	0.09904	0.08037	
$F_2$	0 0 1 0	3019.49	3019.49	−0.01835	$z$	$a$	0.03178	0.00938	0.0085
$F_2$	0 0 0 3	3870.49	3870.49	0.00030	$z$	$a$	0.00052	0.000004	
$F_1$	0 0 0 3	3920.51	3920.15	−0.00034	$x$	$b$	0.00058	0.000005	
$F_2$	0 0 0 3	3930.92	3930.81	−0.00010	$z$	$a$	0.00017	0.0000005	
$F_1$	0 1 0 2	4128.76	4128.73	−0.00367	$x$	$b$	0.00636	0.00066	
$F_2$	0 1 0 2	4142.86	4142.99	−0.00292	$z$	$a$	0.00507	0.00042	
$F_2$	1 0 0 1	4223.46	4223.52	−0.00310	$z$	$a$	0.00536	0.00048	
$F_2$	0 0 1 1	4319.21	4319.43	−0.00142	$z$	$a$	0.00245	0.00010	
$F_1$	0 0 1 1	4322.59	4322.66	−0.00218	$x$	$b$	0.00377	0.00025	
$F_2$	0 2 0 1	4348.72	4348.97	0.01360	$z$	$a$	0.02355	0.00977	
$F_1$	0 2 0 1	4363.61	4363.61	−0.01117	$x$	$b$	0.01934	0.00662	
$F_2$	0 2 0 1	4378.95	4379.15	−0.00081	$z$	$a$	0.00139	0.00003	
$F_1$	0 1 1 0	4537.55	4537.75	−0.05404	$x$	$b$	0.09360	0.16459	
$F_2$	0 1 1 0	4543.76	4543.90	0.05344	$z$	$a$	0.09255	0.16125	
$F_2$	0 0 0 4	5143.24	5143.25	−0.00007	$z$	$a$	0.00011	0.00000	
$F_2$	0 0 0 4	5211.29	5210.65	−0.00011	$z$	$a$	0.00019	0.00000	
$F_1$	0 0 0 4	5230.78	5230.07	0.00003	$x$	$b$	0.00005	0.00000	
$F_2$	0 1 0 3	5370.52	5370.37	−0.00262	$z$	$a$	0.00454	0.00049	
$F_1$	0 1 0 3	5389.67	5389.71	0.00191	$x$	$b$	0.00331	0.00026	
$F_2$	0 1 0 3	5429.58	5429.07	0.00117	$z$	$a$	0.00202	0.00010	
$F_1$	0 1 0 3	5436.79	5436.50	0.00102	$x$	$b$	0.00176	0.00008	
$F_2$	0 1 0 3	5445.12	5444.87	−0.00064	$z$	$a$	0.00110	0.00003	
$F_1$	0 1 0 3	5462.92	5462.74	0.00198	$x$	$b$	0.00343	0.00029	

<sup>a</sup>This ‘experimental’ vibrational intensity of the  $v_2 + v_4$  band [22] correlates with our  $S_{0101F_1}^{(\text{calc})} + S_{0101F_2}^{(\text{calc})} = 0.160 \text{ cm}^{-1} \text{atm}^{-2}$



**Fig. 1.** Vibrational band intensities calculated at  $T = 298.15 \text{ K}$  (filled blue circles) and  $T = 1500 \text{ K}$  (empty red squares) using Eq. (26). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

example, Refs. [18,19]). For higher vibrational order parameters the correspondence between our transition moments and effective dipole moment parameters is less straightforward owing to the complexity of the effective dipole moment operators which are usually given in a tensorial representation.

From the transition moments computed we also generated vibrational band intensities as given by Brown et al. [18], Hilico et al. [19]:

$$S_{\text{vib}} = \frac{8\pi^3 10^{-36}}{3hcQ_v} \frac{LT_0}{T} e^{-E_i/kT} \nu_{if} (1 - e^{-hc\nu_{if}/kT}) \bar{\mu}_{if}^2, \quad (26)$$

where  $\nu_{if}$  and  $E_i$  are the vibrational transition frequency and the lower state energy, respectively, Loschmidt's number

$L = 2.686754 \times 10^{19} \text{ cm}^{-3}$ ,  $T_0 = 273.15 \text{ K}$ ,  $k$  is the Boltzmann constant, and  $Q_v = 1.002$  is the vibrational partition function at  $T = 278.15 \text{ K}$ . Some of the computed values of  $S_{\text{vib}}$  are also illustrated in Tables 1–3, where they are compared to the experimental band intensities from Refs. [19,22,25–27], where available. The agreement is generally very good. In some cases, particularly for combinational bands, there is some ambiguity over how to distribute the individual lines between transitions with the same normal-mode vibrational quantum numbers (see also footnotes to Tables 1–3). This introduces an extra uncertainty into these comparisons.

As an illustration of a possible application of our transition moments, Fig. 1 shows the vibrational band intensities calculated at  $T = 298.15 \text{ K}$  (empty blue squares) and  $T = 1500 \text{ K}$  (filled red circles) using Eq. (26) ( $Q_v = 3.038$  at  $T = 1500 \text{ K}$ ).

## 6. Conclusion

In this work we present new *ab initio* DMSs for  $\text{CH}_4$  which are used to generate the vibrational transition moments and band intensities of  $^{12}\text{CH}_4$  for a large number of vibrationally allowed transitions. These values should be helpful for predicting intensities for individual bands. The dipole matrix elements can also be used for predicting or evaluating effective dipole moment parameters. The analytical representations for the electric dipole moment and potential energy functions of  $\text{CH}_4$  developed in this work have correct symmetry properties of the  $T_d(M)$  group and should be useful for representing similar objects obtained using different methods or levels of theory.

As mentioned above, the vibrational transition moments are less sensitive to the shape of the potential or to the size of the basis set than the (ro-)vibrational energies. For example, using the basis set defined by  $P_{\text{max}} = 10$  and the original *ab initio* PES, we obtain vibrational transition moments that differ by about 0.0002 D on average for transitions involving states below  $6000 \text{ cm}^{-1}$ . Compar-

isons of calculated and experimental (or experimentally derived) band intensities demonstrate the good quality of our new DMSs of CH<sub>4</sub>. We are planning to use these DMSs in calculations of a high temperature line list for methane within the framework of the ExoMol project [78] (see [www.exomol.com](http://www.exomol.com)), which has identified methane as a key target species. Such a line list will be important for modelling molecular opacity in atmospheres of (exo-)planets and brown dwarfs.

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## Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (<http://www.sciencedirect.com>) and as part of the Ohio State University Molecular Spectroscopy Archives ([http://library.osu.edu/sites/msa/jmsa\\_hp.htm](http://library.osu.edu/sites/msa/jmsa_hp.htm)). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jms.2013.05.014>.

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